

## Magnetic field effect on the lifetime of the triplet state of the $F_2$ center in KCl and KBr

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Measurements of the lifetime of the triplet state of the  $F_2$  center in KCl and KBr in a magnetic field and at low temperatures are reported. The results can be quantitatively explained by a phenomenological theory assuming radiative decay; this theory needs only one adjustable parameter  $n$  for each alkali halide studied. Polarization experiments on the phosphorescence of the defects confirm the value of this parameter deduced from the magnetic field experiments. Theoretical calculations of  $n$  using the theory of Silsbee, Farge, and Ortega on radiative decay leads to good agreement with the experiments.

### I. INTRODUCTION

The triplet state of the  $F_2$  center has been intensively studied in the last few years.<sup>1-10</sup> In particular, it has been experimentally proved<sup>9</sup> that the deexcitation process is, at least partly, a radiative one at low temperature, with infrared emission being observable in the region 2–10  $\mu\text{m}$  for these centers in KCl, KBr, and KI. Recently a comprehensive theory of the deexcitation processes in a large temperature range has been proposed by Silsbee, Farge, and Ortega,<sup>10</sup> that we will call the SFO theory. From this work, the radiative mechanism is mainly due to the first-order spin-orbit coupling between the ground triplet state and some excited singlet states arising from contributions of the occupied states of the ions surrounding the defect to the wave function of the  $F_2$  center at low temperatures; this radiative mechanism is predicted to be predominant.

The purpose of this article is to present magnetic field experiments on the lifetime of the triplet state of the  $F_2$  centers in KCl and KBr and their interpretation. In addition, so as to examine the plausibility of some of our hypotheses, we have attempted to measure the polarization properties of the infrared luminescence associated with triplet to singlet recombination. In Sec. II, we describe the experimental method which allows the measurement of the lifetime for two different orientations of the magnetic field in relation to the axis of the  $F_2$  center. In Sec. III, we perform the exact calculations giving the dependence of the radiative lifetime versus magnetic field and temperature and introduce one phenomenological parameter  $n$  for each alkali halide, whose physical significance is close to the polarization rate of the luminescence. In Sec. IV, we show that the experimental results can be fitted by a convenient choice of the value of  $n$  obtained by means of the polarization experiments. Finally, in Sec. V, we calculate a

theoretical value of  $n$  using the SFO theory and, show that its variation from one alkali halide to another comes from the heaviness of the ions involved.

### II. EXPERIMENTAL

As it has been pointed out by Farge,<sup>5</sup> there exists two types of triplet in KCl: the "pure" and the "perturbed" triplets with lifetimes 90 and 60 sec, respectively, at liquid-helium temperature. In this paper, we shall discuss only the "pure" case. To obtain pure triplets, it is necessary to use samples with a rather small concentration of defects. This is normally done in two ways: in the first, samples are irradiated at low temperatures ( $-80^\circ\text{C}$ ) with  $\sim 10^7$  rad from a Co  $\gamma$  source; in the second,  $F$  centers of more heavily  $\gamma$ -irradiated samples are agglomerated at room temperature with light of wavelength corresponding to the high-energy side of the  $F$  band. They are then annealed at  $90^\circ\text{C}$  until sufficiently "dilute," i.e., pure,  $F_2$  centers are obtained.

For KBr, where no influence of the  $F$  centers on the triplet lifetime has been observed, the second method gives the highest concentration in  $F_2$  center when agglomeration is conducted at  $-30^\circ\text{C}$ .

With these methods, the samples contain only a negligible quantity of  $F_3$  center, which is a great advantage because quartet state absorption and luminescence lie in the vicinity of those of the  $F_2$  center. The triplet lifetime has been measured by a variation of the method developed by Engström<sup>7</sup> which analyses the linear dichroism induced in the triplet-triplet absorption bands when the triplets are formed by direct polarized excitation of singlet states of the  $F_2$  centers.<sup>5,7</sup> In our experiment, polarized excitation of pumping light, resonant to the  $F_2$   $^1\Sigma_g^- \rightarrow ^1\Pi_u$  transition is utilized to create

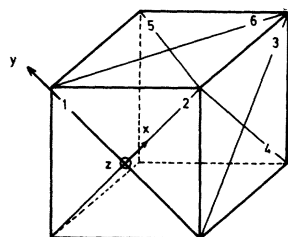


FIG. 1. Six possible orientations of the  $F_2$  centers and our axis convention.

triplets. The efficiency of creation of the triplet excitations is proportional to  $\sin^2\phi$  with  $\phi$  being the angle between the polarization of the light and the axis of the  $F_2$  center. Thus, using samples where the  $F_2$  centers are randomly distributed on the six equivalent  $[110]$  directions of the crystal (Fig. 1), the pumping light induces in the sample a transient linear dichroism, its magnitude being correlated to the number of triplet states in one or several particular orientations.

In order to perform our magnetic field experiments, we have used two different configurations:

(i) In the first configuration, labelled as "[110] configuration" (Fig. 2), the probe light propagates along  $[001]$  and its polarization vector is modulated between  $[1\bar{1}0]$  and  $[110]$ . The pumping light is polarized along  $[110]$ . The  $F_2$  center lying along the direction labelled as 1 are excited into its triplet state while the ones along 2 are not. The triplets along 3, 4 and 5, 6 are equally populated and will give no contribution to the dichroism. Thus, in this configuration, only 1 defects contribute to the linear dichroism.

(ii) In the second configuration, the "[100] configuration" (Fig. 3), the polarization of the probe light, propagates along  $[001]$  and is modulated between  $[100]$  and  $[010]$  when the polarization of the pumping light is along  $[100]$ . The centers 1 and 2 are equally populated, in terms of triplet states, and will not give any contribution to the dichroism. The centers marked 5, 6 are more populated than those marked 3, 4; the resulting dichroism is related to the difference of their population.

These conclusions are true whatever the nature,  $\sigma$ -like or  $\Pi$ -like of the triplet to triplet absorption corresponding to the probe light.

In our experiments, the probe light was modulated by means of the now well-known electro-optical modulator developed by Jasperson and Schnatterly<sup>11</sup> and Kemp.<sup>12</sup> The circularly polarized light, alternatively left and right, produced by this device became linearly polarized by passing it through a quarter wave plate.

With the magnetic field collinear to the probe light ( $[001]$  direction), by turning through  $\frac{1}{2}\pi$

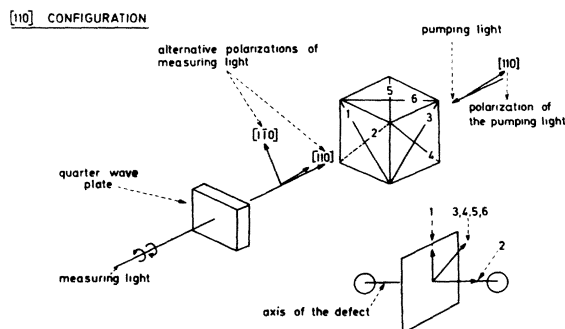


FIG. 2. Configuration "[110]". The polarization of the pumping light relative to  $F_2$  centers is also shown.

the quarter wave plate and the direction of polarization of the pumping light, we pass from the configuration  $[110]$  to the  $[100]$  one: the lifetime of the triplet state of the  $F_2$  center versus to different orientations of the magnetic field can thus be measured simply. Summarizing: (a) In the  $[110]$  configuration, triplet defects which are observed have the magnetic field axis along their  $z$  axis with our axis convention (Fig. 1); (b) In the  $[100]$  configuration for the defect that we measured  $H_z=0$ ,  $H_x=\pm H_y=H/\sqrt{2}$ ,  $H$  being the magnitude of the magnetic field.

The experimental setup is shown in Fig. 4. An M20 type Jobin-Yvon monochromator selected a line of 4-nm bandwidth around the wavelength of 685 nm which corresponds to the main triplet-triplet absorption band in KCl and which lies close to the 675-nm triplet-triplet absorption band in KBr so that we used the same quarter wave plate for both alkali halides. An appropriate attenuator filter avoided the effect of "depumping" the triplet state.<sup>3</sup> For the pumping light, linearly polarized, we used yellow line of a Mercury light source for KCl and green lines for KBr. Appropriate interference filters were placed in order to avoid superposition of orders on the photomultiplier.

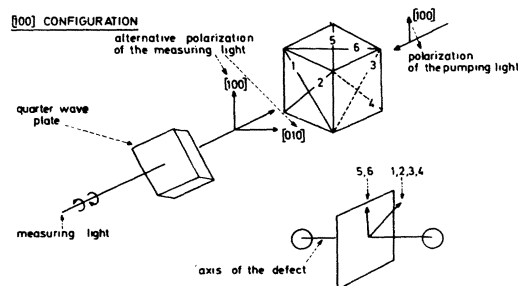


FIG. 3. Configuration "[100]". The polarization of the pumping light relative to  $F_2$  centers is also shown.

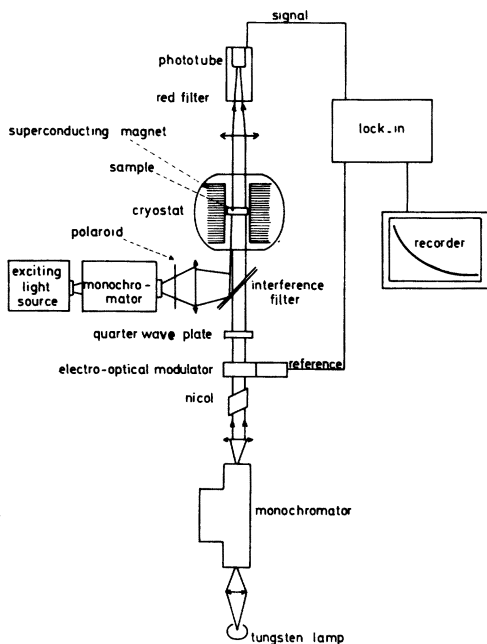


FIG. 4. Apparatus used in measuring the triplet state lifetime under magnetic field.

A feedback circuit<sup>7</sup> on the phototube high voltage permitted us to measure directly the quantity

$$s = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}),$$

with

$$I_{\parallel} = e^{-(\alpha + \delta\alpha_{\parallel})t}, \quad I_{\perp} = e^{-(\alpha + \delta\alpha_{\perp})t},$$

$\alpha$  being the optical constant of the sample before it has been "pumped," and

$$\delta\alpha_{\parallel} = n_{\parallel}e^{-t/\tau}, \quad \delta\alpha_{\perp} = n_{\perp}e^{-t/\tau}.$$

$n_{\parallel}$  and  $n_{\perp}$  are the numbers of triplets in the corresponding directions weighted by the quantity  $\cos^2\theta$ ,  $\theta$  being the angle between the measuring light and the polarization axis of the corresponding triplet-triplet transition, and  $\tau$  is the lifetime.

For small polarization rates, as in our experiments,

$$s \approx \frac{1}{2}(n_{\perp} - n_{\parallel})e^{-t/\tau}.$$

Thus a logarithmic plot of the decaying part of the recorded signal gives a straight line whose slope is the inverse of the lifetime  $1/\tau$  (Fig. 5).

The polarization properties of the radiative emission has been also studied with the apparatus described in Ref. 9. Conventional HR Polaroid filters could be inserted in the helium bath between the sample and the detector, so that polarized phosphorescence of the triplet state in KCl can be monitored directly.

### III. THEORY

We shall develop a phenomenological theory of the effect of the magnetic field. This method is analogous to that developed by McGlynn *et al.* for organic molecules.<sup>13</sup>

The  $F_2$  center, consisting of two electrons trapped on two nearest-neighbor halogen ion vacancies, is roughly equivalent to a hydrogen molecule imbedded in a dielectric medium.<sup>14</sup> One can label its energy levels in terms of molecular spectroscopy in which each level transform according to the irreducible representations of the  $D_{\infty h}$  group. A more detailed analysis must take into account the real symmetry of the potential which is  $D_{2h}$ .  $D_{2h}$  has only non-degenerate irreducible representations. Hence the degeneracy of the  $\pi$  states is lifted as it has been observed experimentally for the singlet to singlet transitions.<sup>15</sup> A realistic scheme, using both notations, is represented on the Fig. 6, after Engström,<sup>8</sup> for KCl. It includes only the orbital part of the wave functions.

The SFO mechanism for the radiative decay involves a weak spin-orbit coupling between the fundamental triplet state  ${}^3\Sigma_u$  and, for example, one of the excited  ${}^1\Pi_u$  singlet states. The perturbed triplet state  ${}^3\Sigma'_u$  becomes

$$|{}^3\Sigma'_u\rangle = |{}^3\Sigma_u\rangle + \frac{\langle{}^3\Sigma_u|\mathcal{H}_{so}|{}^1\Pi_u\rangle}{E({}^1\Pi_u) - E({}^3\Sigma_u)} |{}^1\Pi_u\rangle$$

and the transition probability

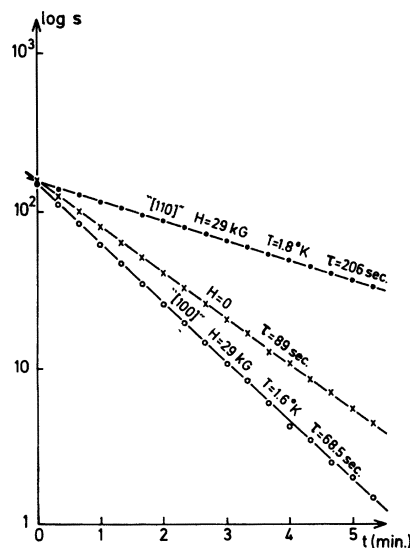


FIG. 5. Logarithmic plot of the transient dichroism for various values of magnetic field and temperature in KCl. As expected the lifetime at  $H=0$  does not depend on the temperature for  $T < 4^\circ\text{K}$ .

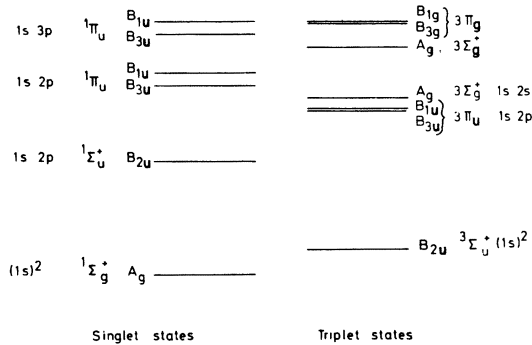


FIG. 6. Energy levels of the  $F_2$  center in KCl after Engström (Ref. 8).

$$K \propto |\langle \uparrow \Sigma_g | \vec{r} | \uparrow \Pi_u \rangle \langle \uparrow \Pi_u | \mathcal{H}_{so} | \uparrow \Sigma_g \rangle|^2.$$

We must now take into account the three sublevels of the fundamental triplet. In  $D_{2h}$  symmetry, inclusion of the spin in the energy scheme, leads to multiplication of each singlet level by  $A_g$  leaving them unchanged. For triplet levels, we must multiply by  $B_{3g}$ ,  $B_{2g}$ , and  $B_{1g}$  which transform, respectively, as the three components  $S_x$ ,  $S_y$ , and  $S_z$  of the total spin.

The three sublevels of the fundamental triplet are then  ${}^3B_{1u}$ ,  ${}^3A_u$ , and  ${}^3B_{3u}$ . The transition probability, for admixing with a singlet excited state  $|\chi\rangle$  becomes proportional to

$$k \propto |\langle A_g | \vec{r} | \chi \rangle \langle \chi | \mathcal{H}_{so} | {}^3B_{1u}, {}^3A_u, {}^3B_{3u} \rangle|^2.$$

The three components of the vector  $\vec{r}$ ,  $x$ ,  $y$ , and  $z$ , transforming as  $B_{3u}$ ,  $B_{2u}$ , and  $B_{1u}$ ,  $|\chi\rangle$  must be a  ${}^1B_{3u}$ ,  ${}^1B_{2u}$ , or  ${}^1B_{1u}$  level for nonvanishing results. The spin-orbit Hamiltonian  $\mathcal{H}_{so}$  transforming as  $A_g$ ,  $|\chi\rangle$  must be a level belonging to the same irreducible representation as the triplet sublevel considered. Hence only two terms are nonvanishing corresponding of the deexcitation of  $B_{3u}$  and  $B_{2u}$  triplet sublevels defined as

$$k_x \propto |\langle A_g | x | {}^3B_{3u} \rangle \langle {}^1B_{3u} | \mathcal{H}_{so} | {}^3B_{3u} \rangle|^2, \quad (1)$$

$$k_z \propto |\langle A_g | z | {}^1B_{1u} \rangle \langle {}^1B_{1u} | \mathcal{H}_{so} | {}^3B_{1u} \rangle|^2. \quad (2)$$

The same argument may be developed for transitions involving spin-orbit coupling between the ground singlet level and some excited triplet level of total symmetry  $A_g$ . Finally, one can attribute a radiative deexcitation probability for each of the fundamental triplet sublevels:  $k_x$  for  ${}^3B_{3u}$ ,  $k_z$  for  ${}^3B_{1u}$ , and zero for  ${}^3A_u$ , because  $A_g - A_u$  transitions are electric dipolar forbidden.

Seidel and Wolf<sup>16</sup> have studied by electron spin resonance (ESR) and electron-nuclear double resonance (ENDOR) the fine structure of the

ground triplet state in KCl. They found terms corresponding to internal magnetic fields of the order of 100 G. These terms are very small in the range of temperature and magnetic field we have used in our experiments and will be neglected here. On the absence of an internal magnetic field, the three triplet sublevels are nearly degenerate and equally populated. The observed lifetime  $\tau_0$  is

$$1/\tau_0 = k_0 = \frac{1}{3}(k_x + k_z).$$

Since, the  ${}^1B_{3u}$  and  ${}^1B_{1u}$  states are nondegenerate for both  ${}^1\Pi_u$  levels (Fig. 6) which can be involved in the transition  $k_x \neq k_z$ . We can use as an adjustable parameter the quantity

$$n = k_x/k_z. \quad (3)$$

$K_0$  being experimentally known,  $k_x$  and  $k_z$  are determined by

$$k_x = [3n/(n+1)]k_0, \quad k_z = [2/(n+1)]k_0. \quad (4)$$

It follows from expressions (1) and (2) that the infrared luminescence emitted by an  $F_2$  center, corresponding to the triplet-singlet transition should be polarized in the plane perpendicular to the axis center, the ratio between the intensities emitted with the polarizations  $x$  and  $z$  being the parameter  $n$ .

Let us now discuss the effect of an applied magnetic field which mixes the three triplet sublevels. Let  $\alpha$  and  $\beta$  be the eigenfunctions of the one-electron operators  $s$  and  $s_z$  for the eigenvalues  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . The spin functions transforming as  $S_x$ ,  $S_y$ , and  $S_z$  in the  $D_{2h}$  group, for a value of the total spin  $S=1$ , are

$$\theta_1 = (1/\sqrt{2})[\alpha(1)\alpha(2) - \beta(1)\beta(2)],$$

$$\theta_2 = (1/\sqrt{2})[\alpha(1)\alpha(2) + \beta(1)\beta(2)],$$

$$\theta_3 = (1/\sqrt{2})[\alpha(1)\beta(2) + \alpha(2)\beta(1)].$$

One can verify that  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$  are the eigenfunctions for the zero eigenvalue of the operators  $S_x$ ,  $S_y$ , and  $S_z$ . Let  $\psi_{B_{2u}}$  be the orbital part of the fundamental triplet, then the wave functions of the three sublevels are

$$\psi_{3B_{1u}} = \psi_{B_{2u}} \theta_1, \quad \psi_{3A_u} = \psi_{B_{2u}} \theta_2, \quad \psi_{3B_{3u}} = \psi_{B_{2u}} \theta_3.$$

The perturbation Zeeman Hamiltonian is

$$\mathcal{H} = g\mu_B (H_x S_x + H_y S_y + H_z S_z).$$

It must be diagonalized into the basis  $(\theta_1, \theta_2, \theta_3)$ .

For  $(H_z = H, H_x = 0, H_y = 0)$ , one finds for the new spin eigenfunctions

$$|1, +1\rangle = (1/\sqrt{2})(\theta_1 + \theta_2), \quad |1, 0\rangle = \theta_3,$$

$$|1, -1\rangle = (1/\sqrt{2})(\theta_1 - \theta_2).$$

The first number in the key is the total value of

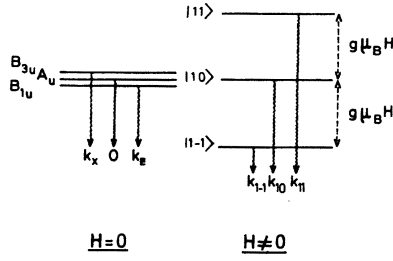


FIG. 7. Decay rate constants of the triplet sublevels with and without magnetic field in KCl.

$S$  and the second is the eigenvalue, for the Hamiltonian  $\mathcal{H}/g\mu_B$ , associated with the eigenfunction.

Hence the fundamental triplet state splits into three levels with the following wave functions:

$$\begin{aligned}\psi_{1,1} &= (1/\sqrt{2})(\psi_{3B1u} + \psi_{3Au}), & \psi_{1,0} &= \psi_{3B3u}, \\ \psi_{1,-1} &= (1/\sqrt{2})(\psi_{3B1u} - \psi_{3Au}).\end{aligned}\quad (5)$$

The rate constants of these levels are easily calculated. From Eqs. (1) and (2), we get

$$k_{1,1} = \frac{1}{2}k_x, \quad k_{1,0} = k_x, \quad k_{1,-1} = \frac{1}{2}k_x.$$

The triplet sublevels are equally spaced by the energy  $g\mu_B H$  (Fig. 7). If they are in thermal equilibrium, we can define a rate constant  $\eta_x$  which is the statistical average of  $k_{1,-1}$ ,  $k_{1,0}$ , and  $k_{1,1}$ :

$$\eta_x = [1/Z(H/T)][k_{1,1} \exp(-g\mu_B H/kT) + k_{1,0} + k_{1,-1} \exp(+g\mu_B H/kT)], \quad (6)$$

with

$$\begin{aligned}Z(H/T) &= \exp(-g\mu_B H/kT) \\ &+ 1 + \exp(+g\mu_B H/kT).\end{aligned}$$

This expression (6) is valid only if  $1/T_1 \gg k_x$ , with  $T_1$  being the spin-lattice relaxation time. In the opposite case, unless only one triplet sublevel is populated by the pumping light, which seems unlikely,<sup>17</sup> one cannot define a single rate constant and the decay signal would no longer be a single exponential. In our case, where  $T_1$  has not been measured, one can see (Fig. 5) a good exponential decay results and thus the preceding condition is well fulfilled. Using Eq. (4) and (6), the rate constant is described by

$$\frac{\eta_x}{k_0} = \frac{3}{2(n+1)} \left( 1 + \frac{(2n-1)}{Z(H/T)} \right). \quad (7)$$

For ( $H_x=0$ ,  $H_x=H/\sqrt{2}$ ,  $H_y=H/\sqrt{2}$ ), one finds similarly

$$\begin{aligned}|1,1\rangle &= \frac{1}{2}(\theta_1 + i\theta_2 + i\sqrt{2}\theta_3), & k'_{1,1} &= \frac{1}{4}k_x + \frac{1}{2}k_x, \\ |1,0\rangle &= (1/\sqrt{2})(\theta_1 - i\theta_2), & k'_{1,0} &= \frac{1}{2}k_x, \\ |1,-1\rangle &= \frac{1}{2}(\theta_1 + i\theta_2 - i\sqrt{2}\theta_3), & k'_{1,-1} &= \frac{1}{4}k_x + \frac{1}{2}k_x.\end{aligned}$$

It is obvious from these expressions that for  $H_x = -H_y$ ,  $k'_{1,1}$ ,  $k'_{1,0}$ , and  $k'_{1,-1}$  are unchanged. Thus the lifetimes of the centers labeled by 3, 4, and 5, 6 in the part II are identical. The resulting rate constant  $\eta_{xy}$  is:

$$\frac{\eta_{xy}}{k_0} = \frac{3}{2} \frac{2n+1}{2n+2} \left( 1 - \frac{2n-1}{2n+1} \frac{1}{Z(H/T)} \right). \quad (8)$$

The parameter  $n$ , defined by (3), must have the same numerical value for both (7) and (8), in each alkali halide.  $\eta_x$  and  $\eta_{xy}$ , defined by (7) and (8), are exact expressions for the radiative decay time constants in the configuration "[110]" and "[100]" defined above.

#### IV. RESULTS

In this section we review our previous measurements. Then we present our present magnetic field measurement in view of this theory and lastly we examine our polarization experiments.

In previous experiments (6), we have studied the lifetime of the  $F_2$  centers under magnetic field by measuring the transient absorption due to the triplet state. For the "pure"  $F_2$  centers no variation was observed. In fact, the decay of randomly distributed triplet states under magnetic field is not, after Sec. III, exponential. In these experiments, we measured in fact an average  $\bar{\eta}$  over the different lifetimes. The experimental uncertainty connected to these measurements was also somewhat large; because the number of defects with the decay efficiency  $\eta_{xy}$  is twice the number with  $\eta_x$

$$\bar{\eta} = \frac{1}{3}(\eta_x + 2\eta_{xy}).$$

From Eqs. (7) and (8), it follows that

$$\bar{\eta} = k_0,$$

thus our theory is consistent with these previous measurements.

In order to obtain lifetime variations as large as possible, the actual measurements have been performed between 1.8 and 4.2 °K with magnetic fields from zero to 30 kG. The observed effects on the lifetime are rather large particularly in KCl where the lifetime varies from 90 sec to about 250 sec in the [110] configurations and from 90 to 70 sec in the [100] configuration.

These variations (Figs. 8 and 9) can be very well fitted by our theoretical expressions (7) and (8) by choosing appropriate values of  $n$ :

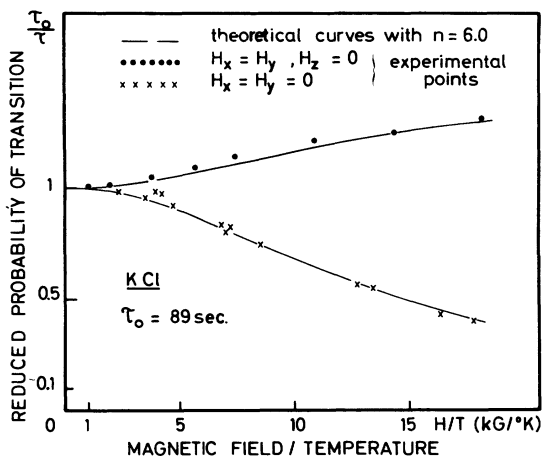


FIG. 8. Behavior of the decay time constant in KCl vs  $H/T$ .

$$n = 6.0 \pm 0.1 \text{ for KCl,}$$

$$n = 1.33 \pm 0.05 \text{ for KBr,}$$

with  $g = 2$ .

In order to test the reliability of this interpretation, we have attempted to measure the polarization properties of the triplet-singlet phosphorescence. Because of the ease with which one can create large concentrations of  $F_2$  centers in KCl, we have worked with this alkali halide. For this purpose, we have used slabs cut parallel to a (110) plane and fixed the cryostat in such a way that the detector receives light emitted along a [110] direction (Fig. 10).

The theory predicts that the light emitted by the center can be polarized only along the  $x$  and  $z$  directions, the ratio between the  $x$  and  $z$  polarizations being the parameter  $n$ .

Since the "pure" triplet state in KCl is excited directly by the pumping light,<sup>5</sup> we used samples with randomly distributed  $F_2$  centers. By creating the triplet state by linearly polarized light of wavelength corresponding to the  $^1\Sigma_g - ^1\Pi_u$  absorption of the  $F_2$  center: (i) first, with vertically polarized light: the centers along directions of type 1 are not excited although centers 2 are (Fig. 10); (ii) with an experiment repeated with horizontally polarized pumping light: then the centers along 1 will be excited and the centers along 2 will not.

The detector receives both  $x$  and  $z$  components of the phosphorescence emitted by the centers of type 1, but only the  $z$  component from centers of type 2. Thus, the efficiency of centers of type 1 being 1, the efficiency for centers of type 2 is

$$I_z / (I_z + I_x) = 1 / (n + 1) = \frac{1}{7}.$$

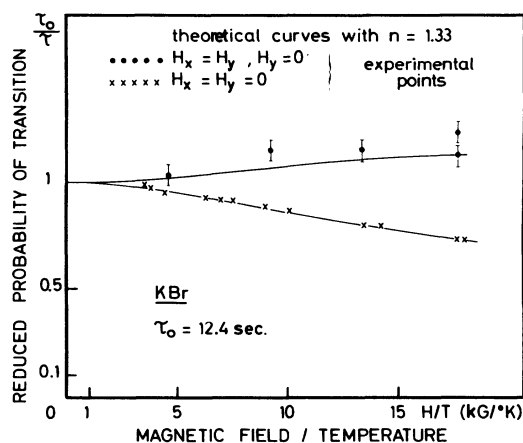


FIG. 9. Behavior of the decay time constant in KBr vs  $H/T$ .

For both cases, by pumping until saturation of the number of triplets, the centers along 3, 4, 5, and 6 are excited and the corresponding luminescence reaches the detector with an efficiency of  $\sim \frac{1}{2}$ . Hence the ratio  $\rho$  of the detected intensities in the two configurations must be

$$\rho = (4 \times \frac{1}{2} + \frac{1}{7}) / (4 \times \frac{1}{2} + 1) \cong 0.72.$$

Our measured value is found to be  $\rho = 0.8 \pm 0.05$ .

However, it is not certain that our triplets were excited entirely by a direct creation process. Moreover the relative efficiency that we attributed to the different orientations of the centers is only an approximation since the solid angle under which the detector sees the sample is not zero; the experimental results can be considered as in qualitative agreement with our prediction.

To measure the value of the parameter  $n$  directly,  $F_2$  centers were "aligned" along the 1 direction with the 4765-Å polarized line of an argon laser at 77 °K. Then we obtained much more lumines-

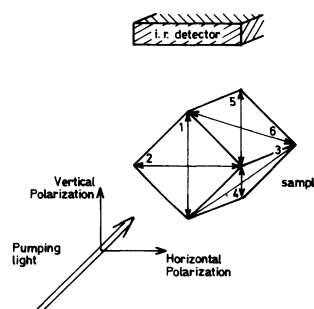


FIG. 10. Schematic arrangement for the ir measurements.

cence signal by inserting between the sample and the detector an infrared polarizer along the  $x$  direction, relative to 1 centers, than inserting it along the  $z$  direction, as predicted. Taking into account the polarization rate of the defects we estimated a value of  $n \approx 4$ . Unfortunately, with this technique to align  $F_2$  centers, we obtained only perturbed triplets whose emissions processes can be different. However this result confirms the magnitude of our prediction from magnetic field interpretation. The case of perturbed triplets will be discussed elsewhere.

### V. DISCUSSION

This section is devoted to a discussion of our results in view of the SFO theory and to the calculation of some quantities of interest with this theory.

The complete expression of SFO for the decay time constant is

$$k^i = k_R^i + k_{NR}^i \quad (8')$$

$k_i$  being the decay rate for the sublevel  $i=x, y, z$ .  $k_R^i$  is the radiative contribution examined in Sec. III and  $k_{NR}^i$  a nonradiative one originating, at low temperature, from the nonadiabatic part of the Hamiltonian.

The interpretation of our data must take into account the nonradiative contribution. However, this contribution is certainly weak: the ratio  $k_{NR}/k_R$  of the resulting lifetime has been estimated by SFO to be 0.05 for KBr and 0.15 for KCl and thus they do not greatly affect the calculation of Sec. III. Further, the part named  $N_1$ , in the SFO article, of the nonradiative contribution involves the same spin-orbit coupling as in the case of the radiative one. Therefore the related rate

constants of the different triplet sublevels are in the same ratios as radiative ones, and the theory developed in Sec. III is not affected. For the part called  $N_2$ , we note that a mode of vibration of  $A_u$  symmetry does not affect the spatial positions of ions located on the symmetry axis of the  $F_2$  center. Thus, even in this case, the rule  $K_y=0$  is valid. Only the value of our parameter  $n$  will be slightly affected by this term.

Thus in general our expressions (7) and (8) are justified (Figs. 9 and 10), explaining the good fit obtained in our magnetic field experiments data. The value of  $n$  in fact can be calculated by the SFO theory of the radiative decay. In this model, calculation of the rate constants involves spin-orbit coupling originating from admixture in the  $F_2$ -center wave functions of  $p$ -like orbitals on surrounding ions. The spin-orbit coupling matrix element is the sum of two terms, one from admixture of wave functions of the two halogen ions along the axis of the defect and the second of the two  $K^+$  ions located in sites labelled by 1 and 2 in Fig. 11. The contributions of the others nearest-neighbor  $K^+$  ions cancel by symmetry. SFO have calculated the spin-orbit coupling between the  ${}^3B_{3u}$  and  ${}^1B_{3u}$  levels:

$$\langle {}^1B_{3u} | \mathcal{H}_{so} | {}^3B_{3u} \rangle \approx C \{ \langle s_A | s_B \rangle \sqrt{2} [p'(a)/s'(a)] \Lambda_{K^+} + [p(a\sqrt{2})/a\sqrt{2} s'(a\sqrt{2})] \Lambda_{X^+} \}, \quad (9)$$

with  $s(r)$  the ground-state wave function of the  $F$  center,  $p(r)$  the first excited-state wave function of the  $F$  center, the prime index refers to the first derivative of these wave functions,  $a$  is the anion-cation distance,  $\Lambda_i = Z_i b_i / g_i$ ,  $Z_i$  is the effective nuclear charge of the ion  $i$ ,  $g_i$  is the nuclear  $g$  value of the ion  $i$ ,  $b_i$  is the anisotropic-hyperfine-structure value on the ion  $i$  for the  $F$  center,  $\langle s_A | s_B \rangle$  is the overlap integral of two  $s$ -like wave functions centered on vacancies  $A$  and  $B$  (Fig. 11), and  $C$  is a numerical factor.

Using the SFO procedure, we have calculated the spin-orbit coupling between  ${}^1B_{1u}$  and  ${}^3B_{1u}$ :

$$\langle {}^1B_{1u} | \mathcal{H}_{so} | {}^3B_{1u} \rangle \approx C \{ \langle s_A s_B \rangle \sqrt{2} [p(a)/as'(a)] \Lambda_{K^+} + [p(a\sqrt{2})s'(a\sqrt{2})] \Lambda_{X^+} \}. \quad (10)$$

In order to estimate the value of  $n$  we have adopted the following values:

(a)  $s(r)$  and  $p(r)$  are the Gourary and Adrian's<sup>18</sup> type-I ground- and excited-state wave functions.

(b)  $\langle s_A | s_B \rangle \approx 0.4$ , from emission measurements of the triplet state.<sup>19</sup>

(c) The ratio of the coefficients of  $\Lambda_{K^+}$  for the  ${}^3B_{3u}$  and  ${}^3B_{1u}$  terms,  $ap'(a)/p(a)$ , is in fact the ratio of the  $S_v$  to the  $S_r$  integrals as defined by Smith.<sup>20</sup> Thus we have adopted Smith's value

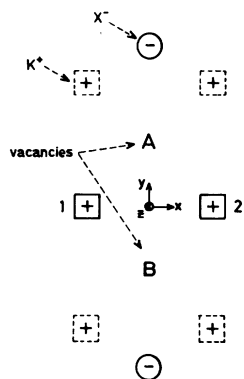


FIG. 11. Spatial repartition of the ions involved in the spin-orbit coupling leading to the decay of the triplet state of the  $F_2$  center.

$$S_o/S_r \approx 2. \quad (11)$$

(d)  $b_i$  is given by the ENDOR data reviewed by the article of Seidel and Wolf.<sup>16</sup>

Finally, from Eqs. (1)–(3), (9), and (10), one obtains

$$n_{\text{KCl}} \approx 2.8.$$

In order to obtain a theoretical estimate of  $n$  for KBr, where the Gourary and Adrian's wave functions are not available, we have used the same values of the  $\zeta$  and  $\zeta'$  related parameters, because these parameters change slowly with the interionic distance; we obtain

$$n_{\text{KBr}} \approx 1.6.$$

These values are in good agreement with the empirical value. Thus the physical meaning of the value of  $n$  becomes apparent.  $n > 1$  comes from the detailed structure of the  $F_2$  center; the symmetry plane perpendicular to the defect axis contains two next-neighbor  $K^+$  ions in the  $x$  direction and none in the  $z$  direction. Hence the spin-orbit coupling is always larger along the  $x$  direction than along the  $z$  direction. The variation of  $n$  between KCl and KBr is due to the different strength of the spin-orbit coupling on the  $\text{Br}^-$  and the  $\text{Cl}^-$  ions. If the coupling with the halogen ion is larger compared to the coupling with the alkali ion,  $n$  will be smaller. Therefore the  $\text{Br}^-$  ion being much larger than the  $\text{Cl}^-$  ion leads to a smaller  $n$  in KBr than in KCl.

## VI. CONCLUSION

In this paper, we have presented measurements of the lifetime of the triplet state of the  $F_2$  center in KCl and KBr under strong magnetic field and at low temperatures for two different orientations of the field versus the defect. The observed lifetime shows large variations which can be well fitted by a phenomenological theory that we have developed here, leading to a general expression of

the lifetime with only one adjustable parameter  $n$ . By studying the polarization properties of the phosphorescence in KCl, we have justified both the physical assignment and the order of magnitude of  $n$ . A theoretical value of  $n$  using the SFO theory of the radiative decay has also been calculated. We can conclude from our results the following:

(a) Part of the magnetic field behavior is due to the fact that a radiative  $A_g \rightarrow A_u$  transition is forbidden for group-theoretical reasons. It follows that no light, polarized in a parallel direction to the axis of the defect, can be emitted in the triplet-to-singlet phosphorescence.

(b) The other cause of the magnetic field behavior is the fact that  $n \neq 1$ . This is due to the symmetry of the  $F_2$  center and the magnitude of this effect is governed by the ratio of the spin-orbit coupling strengths between the halide and the alkali ion. The phosphorescence emitted along the axis of the defect is polarized,  $n$  being the ratio between the  $x$  and  $z$  components.

With the SFO theory, we have calculated a theoretical value of  $n$  in the case of a spin-orbit coupling between the ground triplet state and one ( $^1\Pi_u$ ) of the excited singlet state which leads to a good agreement with the experimental observations. Therefore the SFO theory accounts for the main features of the radiative decay of the  $F_2$  center in KCl and KBr. Further investigation of the triplet decay mechanism would be possible by studying, for example, the influence of various impurities on the lifetime of  $F_2$  centers in their triplet state. In particular, the  $F_{2A}$  center, consisting of a perturbed  $F_2$  center, analogous to the  $F_A$  center,<sup>21</sup> would be of some interest.

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